PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:

Hisashi AMAYA et al. | Art Unit: 1742

Application No.: 10/798,855 | Examiner: Roe, J. R.

Filed: March 12, 2004 | Attorney Dkt. No.: 12054-0024

For: MARTENSITIC STAINLESS STEEL

DECLARATION UNDER 37 C.F.R. 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Hisashi Amaya, do hereby declare as follows:

1) I have been employed by Sumitomo Metals Industries, Ltd., (SMI) who is the owner of the above-captioned patent application (the Application), since April 1st, 1991. I have had various positions in SMI, and my current position is Material R&D Group Manager, Pipe & Tube Technology Section, Quality Control & Technical Service Department, Wakayama Steel Works. As a result of my experience and current position in SMI, I am very knowledgeable regarding steel pipes and their manufacture, and particularly with steel pipes for use in oil and natural gas drilling applications.

2) I am familiar with the content of the Application and its prosecution at the U.S. Patent and Trademark Office, and especially the Advisory Action dated December 11,

2008 and the comments stated therein, and the final Office Action of September 26, 2008 and the final rejection stated therein.

3) I am also familiar with the prior art now being used to reject the claims of the application, United States Patent Nos. 5,858,128 to Miyata et al. (Miyata) and 5,716,465 to Hara et al. (Hara). In the rejection, the Examiner admitted that the claim limitations regarding the hardness being 30 – 45 in HRC and the amount of carbides in grain boundaries of the prior austenite being not more than 0.5 volume % (the "claim limitations at issue") are not present in the cited prior art of Miyata and Hara. Nevertheless, the Examiner has taken the position that the composition and processing of Miyata and Hara are similar to that of the invention such that these claimed characteristics are expected. This Declaration is made to demonstrate that the processing of each of Miyata and Hara is not similar to that employed by the invention so as to produce the claim limitations at issue and the assumption that these limitations can be expected is improper.

4) The characteristics of the process that the claimed martensitic steel requires involve two different processing scenarios. A first scenario is that an ordinary or conventional tempering treatment is omitted so as to allow the steel to be made in an as-quenched condition. The second scenario is that a low temperature tempering step is conducted at 400 °C or less. The purpose of using one of these two scenarios relates to what happens to the steel during conventional tempering. An ordinary tempering temperature causes precipitation of carbides at the prior austenite grain boundaries and

this precipitation results in a loss of strength of the steel. The specification teaches these alternatives in paragraphs [0074], [0075], and [0076]wherein it is stated:

> [0074] The martensitic stainless steel according to the invention may be obtained through a process in which steel having a specified chemical composition is hot worked and then a predetermined heat treatment is applied thereto. <u>For instance, a steel material is heated in a temperature of the Ac_3 point or more, and then cooled by the quenching or air cooling (slow cooling) after hot worked</u>. (emphasis added)
>
> [0075] <u>Alternately, the above treatment is applied to the steel material and it is thus cooled down to room temperature, and subsequently the steel material is quenched or air cooled in the final treatment, after again heating it at a temperature of the Ac_3 point or more</u>. The quenching often provides too much increase in the hardness and a reduction in the toughness, so that the air cool is preferable to the quenching. (emphasis added)
>
> [0076] After cooled, the tempering can be applied in order to adjust the mechanical strength. However, the tempering at a high temperature provides not only a reduction in the mechanical strength of the steel, but also an increase in the amount of the carbides in the grain boundaries of the prior austenite, thereby causing the localized corrosion to be induced. In view of this fact, <u>it is preferable that the tempering should be carried out at a low temperature of not more than 400 °C</u>. The hot work in the above treatments means the forging, plate rolling, steel pipe rolling or the like, and the steel pipe described herein means not only a seamless steel pipe but also a welded steel pipe. (emphasis added)

5) Despite the teachings of the specification, the Examiner has taken the position that the processing of Miyata and Hara is similar to the claimed processing such that the claim limitations at issue are expected. More particularly, the tempering temperature employed in each of Miyata and Hara is 550 °C. The instant specification shows a comparative example wherein the tempering temperature is 600 °C. Because Miyata and Hara use a different tempering temperature than the comparative example from the instant specification (600 °C v. 550 °C), the Examiner has taken the position that the tempering at 550 °C can be more like the low temperature tempering scenario (2)

discussed above (400 °C or less) and therefore the claim limitations at issue can still be present.

6. The purpose of this Declaration is to submit evidence showing fundamental metallurgical principles so as to demonstrate that the 550 °C tempering temperature used in both Miyata and Hara is representative of conventional tempering and the effects thereof. Because the tempering temperature used in Miyata and Hara is representative of conventional tempering, it produces a conventional result, which cannot be said to be the same or even similar to the claim limitations at issue.

7. Submitted herewith are Exhibits A and B, which are technical literature, to demonstrate that tempering the material of the invention at 550 °C produces a steel product that is fundamentally different from a steel product that is subjected to a tempering temperature of 400 °C or less.

8. Exhibit A is an excerpt from "Data Book for Stainless Steel", page 72 thereof along with the appropriate translation thereof. This page lists Figure 2.13, which is a Time-Temperature-Transformation Curve of SUS 410 (0.1%C – 12% Cr) with an equivalent Cr content to that of the claims before the Examiner. A vertical axis of the diagram indicates temperature in degrees Centigrade (°C) and a horizontal axis indicates time(s) with a logarithmic scale. Legend symbols A, F, and C represent austenite, ferrite, and carbide, respectively. The text associated with Figure 2.13 is the subject matter of the translation of Exhibit A.

As a general trend, Figure 2.13 shows that there exists a precipitation nose where austenite + ferrite + carbide precipitate at about 700 °C. The precipitation

region still stands at 550 °C whereas a typical C shaped curve is exhibited. This graph also shows a zone of 400 °C or less, which is beneath the C-shaped curve, and which can be considered to be free from carbide precipitation as long as a commercially common duration of time is taken.

The martensitic stainless steel of the invention comprises mainly a martensitic structure in an as-quenched condition wherein precipitation of carbides is inhibited, although there may be some cases where retained austenite may be partially exist depending on the alloy composition. Referring again to Figure 2.13 of Exhibit A, a heat treatment, i.e., tempering, in the temperature range of 500-700 °C should incur precipitation of carbides. This contrasts with a heat treatment in a temperature range of 400 °C or less, wherein I, as one of skill in the art, would interpret Figure 2.13 to teach that a steel product is produced that does not have the carbide precipitation that occurs when the same steel product is tempered in the temperature range of 500-700 °C. A product subjected to a heat treatment in a temperature range of 400 °C or less is more similar to a steel product in an as-quenched condition than one that has carbide precipitation as a result of tempering in the range of 500-700 °C.

One reason for this change in the steel product characteristic when subjected to heating in a range of 500-700 °C versus 400 °C or less relates to the diffusion rate of carbide-forming elements. That is, the diffusion rate of carbide-forming elements carries much weight and because of the importance of the diffusion rate, at a lower temperature, i.e., 400 °C or less, almost no diffusion of carbide-forming elements takes place. The Examiner's attention is directed to the following website, which has relevant

information regarding carbide precipitation, http://steel.keytometals.com/Articles/Art128htm. Relevant information from this website is reproduced below as follows:

> A number of the familiar alloying elements in steels form carbides, which are thermodynamically more stable than cementite. It is interesting to note that this is also true of a number of nitrides and borides. Nitrogen and boron are increasingly used in steels in small but significant concentrations. The alloying elements Cr, Mo, V, W, and Ti all form carbides with substantially higher enthalpies of formation, while the elements of nickel, cobalt, and copper do not form carbide phases. Manganese is a weak carbide former, found in solid solution in cementite and not in a separate carbide phase.

Based on the above, it would be expected that when strong carbide-forming elements are present in the steel in sufficient concentration, their carbides would be formed in preference to cementite. Nevertheless, during the tempering of all alloy steels, alloy carbides do not form until the temperature range 500-600 °C is reached. This is because below this range, the metallic alloying elements cannot diffuse sufficiently and rapidly enough for alloy carbides to nucleate.

9. Exhibit B is an excerpt from the "Handbook for Stainless Steel", page 88 thereof, along with a translation of the relevant parts. This page has Figure 1.51, which shows the relationship between tempering temperature and change of characteristics for a 12% Cr steel. A horizontal axis thereof indicates tempering temperature (°C) and a vertical axis indicates hardness, toughness, and a decrease of corrosion resistance. The hardness is shown in the top section of the graph, with toughness in the middle and a decrease in corrosion resistance in the lower section of the graph. It should be

understood that the decrease in corrosion resistance curve should be interpreted such that when the value on the vertical axis increases, corrosion resistance decreases.

When tempering is carried out for martensitic stainless steels for use in oil well applications, its primary aim is to secure toughness. Thus, the tempering temperature aim is in region III in Figure 1.51. It can also be seen that the value representing a decrease in corrosion resistance increases so that corrosion resistance decreases when improving toughness using tempering. The reason for this has to do with carbide formation, which then causes a generation of Cr-depleted regions. The reason that Miyata and Hara temper at 550 °C is for the same purpose shown in Figure 1.51, i.e., to improve toughness.

Figure 1.51 demonstrates that tempering a 12% Cr steel at 550 °C is more similar to a steel that is tempered at 600 °C than a steel that is heated to a temperature of 400 °C or less. Moreover, Figure 1.51 also shows that the properties of a steel tempered in a range of 500-700 °C are not the same as one subjected to heating at 400 °C or less.

10. To summarize, the objective evidence submitted as part of this Declaration demonstrates two main points as follows: (1) tempering a 12% Cr steel at 550 °C produces characteristics in terms of carbide formation, toughness, and corrosion resistance that are similar to those found in the same steel subjected to a tempering temperature of 600 °C; and (2) that properties in a 12% Cr steel tempered at 400 °C or less would not be expected to be the same as those in a 12% Cr steel tempered at 500-700 °C. Therefore, it is error for the Examiner to conclude that the claim limitations at

issue are expected or present in the steels of Miyata and Hara when their tempering temperatures are fundamentally different than those employed according to the invention to obtain the claimed steels and their properties, especially the claim limitations at issue.

I hereby declare that all statements made herein of my own knowledge are true and that all statement made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application and any patent issued thereon.

Date: March 2, 2009

Hisashi Amaya

Name: Hisashi Amaya

EXHIBIT A

English Translation of Excerpts: Technical Literature No.1

"Data Book for Stainless Steel",
edited by JAPAN STAINLESS STEEL ASSOCIATION,
published by THE NIKKAN KOGYO SHINBUN, LTD.
page 72, Fig. 2.13

Fig. 2.13 Time-Temperature-Transformation Diagram for 0.1C-12Cr Steel
Source: R.L. Ricket, W.F. White, C.S. Walton and J.C. Butler:
Trans. ASM, 44 (1952), p.138

Vertical axis: Left; Temperature, Right; Rockwell Hardness
Horizontal axis: Time (s)

Austenitizing temperature 982℃
Grain Size Number 6~7
A: Austenite
F: Ferrite
C: Carbide

Keywords:
0.1C-12Cr Steel
Time-Temperature-Transformation curve

Remarks:

This is Time-Temperature-Transformation curve for SUS 410 (0.1C-12Cr) which is most widely used amongst various martensitic stainless steels.

Eutectoid transformation point for 12 Cr Steel is about 0.3% C, but depending on whether γ phase is hypoeutectoid or hypereutectoid, precipitation of α phase or carbides precedes pearlite transformation, respectively.

A nose of pearlite transformation lies at about 700℃, but as the C concentration in γ phase becomes higher, the nose temperature becomes lower: see p.101 in Data Book.

ステンレス鋼データブック

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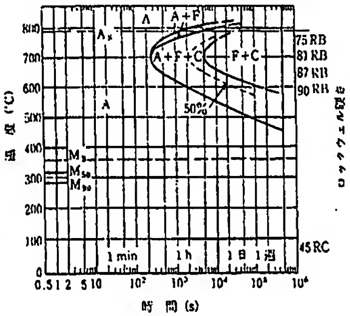

C 0.11　Mn 0.44
Si 0.37　Ni 0.16
Cr 12.18
オーステナイト化温度 982℃
結晶粒度 6～7
A：オーステナイト
F：フェライト
C：炭化物

図2.13　0.1C-12Cr鋼の等温変態図
出典：*R.L.* Ricket, *W.F.* White, *C.S.* Walton and *J.C.* Butler：Trans. ASM. 44 (1952), p.138

図2.13［キーワード］
・0.1C-12Cr鋼
・等温変態曲線

◉データの見方◉

マルテンサイト系ステンレス鋼の中でも，最も広く使用されているSUS 410 (0.1C-12Cr)の等温変態曲線である．

12Cr鋼の共析組成は約0.3%Cであるが，γ相組成が亜共析であるか過共析であるかに従って，α相または炭化物の析出がパーライト変態に先行して生じる．

パーライト変態のノーズは低C側で約700℃であるが，γ相中のC濃度が高いものほどやや低くなる．

→便覧ページ　p.101

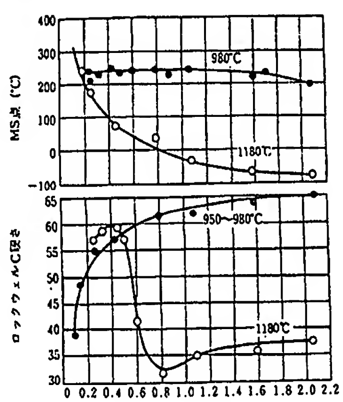

図2.14　13Cr鋼のM_s点，焼入硬さとC含有量との関係
出典：*R.L.* Ricket, *W.F.* White, *C.S.* Walton and *J.C.* Butler：Trans. ASM. 44 (1952), p.138

図2.14［キーワード］
・13Cr鋼
・焼入硬さ
・C量の影響

◉データの見方◉

図中の数字は焼入温度である．

焼入温度の高い1180℃の場合は，0.80%以上のC含有量でM_s点が常温以下に下がり，過冷オーステナイト単相の組織になる．

また，残留オーステナイト量が増すほど焼入硬さも低下する．

→便覧ページ　p.101

2.2.2　フェライト系ステンレス鋼

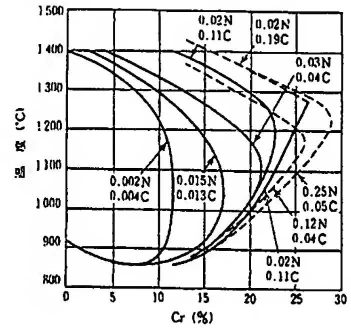

図2.15　Fe-Cr 2元系の$\alpha/(\alpha+\gamma)$境界に及ぼすCおよびN添加の影響
出典：*E.* Baerlecken, *W.A.* Fischer and *K.* Lorenz：Stahl u. Eisen, 61 (1961), p.768

図2.15［キーワード］
・Fe-Cr系状態図
・C量の影響
・N量の影響
・$\alpha/(\alpha+\gamma)$ 境界

◉データの見方◉

Fe-Cr系の$\alpha/(\alpha+\gamma)$境界に対するCとNの影響を示したものである．CとNの増加とともに$\alpha/(\alpha+\gamma)$境界は高Cr側に移動する．普通，フェライト系ステンレス鋼のCr含有量は12～30%であるため，CとNがごく少ない場合は常温から高温までα単相の組織となる．しかし，C，N量が増加するとγループ領域が高Cr側に著しく拡大するため，高温でγ相が生成するようになる．

→便覧ページ　p.103

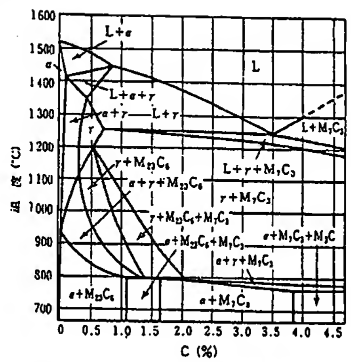

図2.16　Fe-Cr-C 3元系状態図の17%Cr等温度断面図
出典：*K.* Bungardt, *E.* Kunze and *E.* Horn：Arch. Eisenhüttenwes., 29 (1958), p.193

図2.16［キーワード］
・Fe-Cr-C 3元系状態図
・17%Cr等温度断面図

◉データの見方◉

Fe-Cr-C 3元系状態図の17%Crで切断して示した等濃度断面図である．Cを多量に添加すると，高温で安定な組織はα＋炭化物となり，生成する炭化物も量が増加するに従い$M_{23}C_6 \rightarrow M_7C_3 \rightarrow M_3C$と変化する．

→便覧ページ　p.106

英 文 索 引

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EXHIBIT B

English Translation of Excerpts: Technical Literature No. 2

"Handbook for Stainless Steel", Third Edition,
edited by JAPAN STAINLESS STEEL ASSOCIATION,
published by THE NIKKAN KOGYO SHINBUN, LTD.
page 88, Fig. 1.51

1.4.4. HEAT TREATMENT

1) Objects of Heat Treatment

Heat treatment is an important step either at in-process stage or finishing stage for producing stainless steels. For stainless steels, their mechanical properties, formability, magnetic properties, resistance to oxidization and resistance to corrosion resistance are more or less affected by heat treatment.

Fig. 1.51 Change of Properties according to Heating Temperatures

Vertical axis: Top; Increase of Hardness,
Middle; Increase of Toughness,
Bottom; Decrease of Corrosion Resistance

Horizontal axis: Heating Temperature (℃)
As-quench condition

In the figure: High C, Low C

I: Low-Temperature Tempering
II: Not Applicable
III: High-Temperature Tempering
IV: Hardening

ステンレス鋼便覧

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系ステンレス鋼では動的再結晶が起こるという報告もある[6]．動的再結晶が開始するひずみ量（図1.50(b)の ε_r）は，加工温度が低くなるほど，またはひずみ速度が大きくなるほど大きくなる．通常の熱間圧延のようにひずみ速度が大きい場合には，1パス圧下率10〜20％程度では動的再結晶は起こらず，加工硬化組織になる．

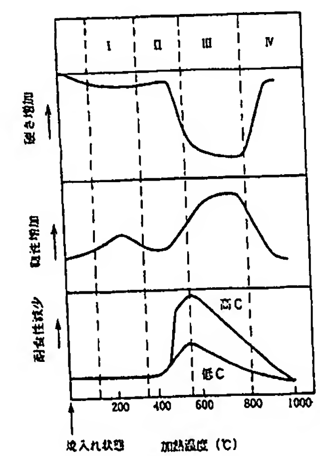
参考文献

1) 冗木弘安，藤村全成：日本金属学会誌，40 (1976)，p.275
2) H.J. McQeen and J.J. Jonas: Plastic Deformation of Materials, ed by R.J. Arsenault (1975), p.393 [Academic Press]
3) 川崎宏一，松尾宗次：鉄と鋼，70 (1984)，p.1808
4) E. Houdremont: Handbuch der Sonderstahlkunde. S. 256 (1956)
5) 牧正志，田村今男：鉄と鋼，70 (1984)，p.2073
6) T. Maki, S. Okaguchi and I. Tamura: Proc. of Int. Conf. on Strengh of Metals and Alloys (ICSMA-6), Ed. by R.C. Gifkins (1982), vol. 1, p.529 [Pergamon Press]

1.4.4 熱　処　理

1) 熱処理の意義

熱処理はステンレス鋼製造の中間工程および最終工程での重要な作業である．ステンレス鋼における機械的性質，成形加工性，磁気特性，耐酸化性および耐食性は，大なり小なり熱処理によって左右される．特にステンレス鋼においては耐食性の確保という点で，熱処理は極めて重要な工程となっている．



I．低温焼戻し　II．利用せず
III．高温焼戻し　IV．硬化

図1.51　12Cr鋼の加熱温度による特性変化

2) 熱処理に関連する金属組織

a) マルテンサイト系

焼入れ，焼戻しはマルテンサイト系ステンレス鋼を中心に行われる熱処理で，焼入れはオーステナイト領域に加熱し，炭化物をオーステナイト中に固溶し，急冷する．焼入れ温度が高いほどオーステナイト中のC固溶量が多くなり，焼入れマルテンサイトは硬くなる．しかし逆に残留オーステナイトが多くなると硬さは減少する．また，この残留オーステナイトが焼戻し後の冷却過程でマルテンサイト化して靭性を害することとなる．このマルテンサイトは焼割れの原因となるので，焼戻しは焼入れ後，なるべく速やかに実施する必要がある．焼戻しは図1.51に示すように硬度や目的によって低温焼戻しか，高温焼戻しのいずれかが行われ，中間の400〜550℃の温度域は焼戻し脆性を生じるため，避けなければならない．

b) フェライト系

フェライト系ステンレス鋼での熱処理は，加工によるひずみ硬化を回復させること，溶接の熱履歴で生じた変質部の焼戻しによる靭性回復のために行うことが多く，一般に高温に加熱し空冷する焼なましが行われる．熱処理の基本的な考え方は，$\alpha+\gamma$ 領域に入ることなく α 単相温度で加熱し，空冷することにある．本系合金では高温加熱による粒界腐食，σ 相脆化，結晶粒粗大化，475℃脆性などの問題が発生することがある．オーステナイト系ステンレス鋼とは逆に焼なまし温度から冷却すると，粒界近傍のCr欠乏層による

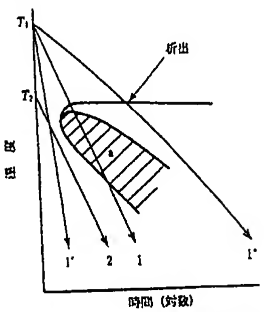


図1.52　フェライトステンレス鋼の粒界腐食に及ぼす冷却速度と加熱温度の影響の模式図[2]
等温時効による Cr 炭化物の析出開始時間と腐敗化領域(a)を示す．冷却方法1が粒界腐食される条件：1'1" および2は粒界腐食されない条件：1" では析出は起こるが鋭敏化は回復している．

粒界腐食を生じるが，徐冷した場合には生じない[1]．これはフェライト中の拡散係数が大きく，急冷でも粒界へのCrの拡散が起こり，徐冷した場合にはさらにCr拡散が進行しCr欠乏層の回復が起こるためである．これらを模式的に示すと図1.52[2]のようになる．また本系合金では700℃前後で長時間加熱されると粒界に σ 相が析出し，耐粒界腐食性が低下したり，耐熱用途においては高温強度の低下を引き起こす．475℃脆性は400〜500℃で長時間加熱したとき現れ，Cr濃度の高い α' 相の生成によると考えられており，特に475℃で最も顕著である．脆性とともに耐食性も劣化する．σ 相脆化については1.6.2項a)で説明する．

本系合金ではフェライトが安定相で変態がないため，熱処理により結晶粒の微細化はできず，高温に加熱すると，結晶粒粗大化による粒界面積の減少のため，単位面積当たりのCr炭化物析出量が多くなり，粒界腐食感受性が高くなる．また，結晶粒の粗大化は絞り加工時，曲げ加工時の肌あれ（オレンジピール）の原因となる．オーステナイト系，フェライト系とも熱間，冷間加工後の加熱により，軟化，再結晶，結晶粗大化も起こるが，再結晶温度，粗大化温度は鋼種，加工量によって異なる[1,3]（図1.53参照）[3]．特にフェライト系ステンレス鋼では加熱による結晶粒の粗大化はオーステナイト系より速く，結晶粒が大きくなりやすいので熱処理に当たっては過熱を避ける必要がある．しかし，最近の本系合金で低C，NとしNb，Tiなどの C，N を固定する元素を含有しているものは，焼きなまし温度から急冷しても鋭敏化されることなく耐粒界腐食性がよく，かつ結晶粒の粗大化も起こりがたい．

c) オーステナイト系

本系合金では，目的により固溶化処理，安定化処理，応力除去焼なまし，時効処理が行われる．

固溶化処理は，耐食性という観点からは腐食の原因となるCr炭化物や窒化物を基地オーステナイト組織へ固溶させることであり，このほかに再結晶，元素の固溶，結晶粒度調整などを目的としている．

図1.54はNi-Cr系ステンレス鋼のCおよびNの固溶度曲線を示したものである．炭化物を完全に固溶させるためには，固溶温度以上に加熱する必要がある．平衡状態におけるCの固溶量はNi量の増大により減少し，高Ni合金になるほど炭化物が生成しやすいことを示している．粒界にCr炭化物または窒化物が析出すると近傍のCr量が欠乏する．Cr欠乏層のCr量は熱力学的な平衡関係により計算も試みられているが，1.7.1項4)-b)で述べる．このようなCr炭化物を少なくするため，Ti，Nbを添加したSUS 321，SUS 347のような安定化ステンレス鋼では，炭化物の安定化を確実にするため，固溶化処理の後に，850〜930℃に加熱，水冷を行う．TiまたはNbでCをTiCまたはNbCとして固定しても，高温になるとこれらの炭化物は分解固溶する．そこで，いったん固溶したCを安定化元素と結びつけるため

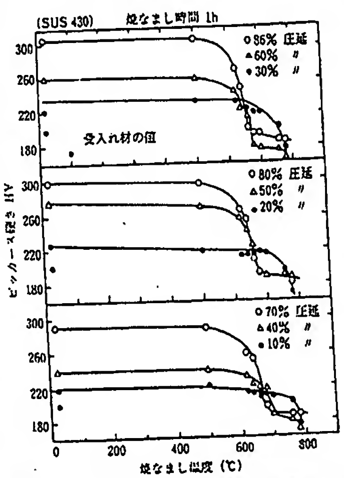


図1.53　400℃で圧延したSUS 430の硬さに及ぼす焼なまし温度の効果[3]

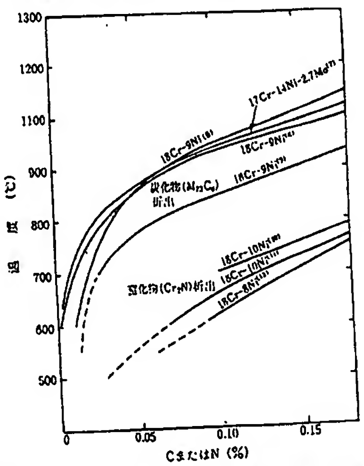


図1.54　ステンレス鋼中のCまたはNの固溶度と温度の関係

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